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Progress toward atomic layer epitaxy of diamond using radical chemistry

by

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PROGRESS TOWARD ATOMIC LAYER OF DIAMOND USING RADICAL CHEMISTRY

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ABSTRACT

A novel method for atomic layer epitaxy (ALE) of diamond using radical reactants under medium vacuum conditions is being developed. Precursor molecules are injected into a stream of thermally-dissociated fluorine atoms, generating radicals in a chemically specific way. We have grown diamond particles at rates of approximately 0.1 $\mu\text{m/hr}$ on polycrystalline copper and nickel wire substrates seeded by diamond particles from continuous flows of F/F_2 , H_2 , and C_2H_2 or CH_4 at substrate temperatures of 500-600 $^\circ\text{C}$ and reactor pressures between 10^{-3} and 10^{-1} Torr. Identification of diamond with submicron lateral resolution was made using electron microprobe x-ray fluorescence wavelength dispersive spectroscopy.

INTRODUCTION

Atomic layer epitaxy (ALE) is a powerful technique for growing materials one atomic layer at a time (1). Originally developed for II-VI materials, ALE has been widely applied to growth of GaAs and other III-V semiconductors. ALE processes for silicon are currently being developed. An ALE process for diamond would have a number of important applications. First, such a process would be useful in diamond microelectronics, permitting the deposition of precisely controlled, extremely uniform, ultrathin, atomically abrupt layers for modulation doped superlattices or heterostructures. Second, the reduced substrate temperature typically associated with ALE (1) could facilitate the achievement of heteroepitaxy of diamond. Finally, very high nucleation densities on nondiamond substrates may be achievable using ALE methods, which should produce very smooth films and would be extremely useful for optical and tribological applications. Selectively-produced radical precursors should offer a number of advantages for growth of group IV materials such as diamond, including significant growth rates at modest temperatures and the maintenance of an adsorbate-terminated sp^3 surface (essential for diamond growth) throughout the ALE cycle, which should minimize interlayer diffusion and contamination.

EXPERIMENTAL METHOD

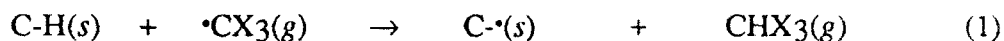
Our method for diamond ALE involves selectively-produced radicals in medium vacuum and should have a number of advantages over more conventional diamond growth techniques. The surface dangling bonds remain capped by hydrogen or halogen atoms throughout the process cycle, stabilizing the diamond surface. Because radical reactions typically have low activation energies, the process should remain viable at relatively low

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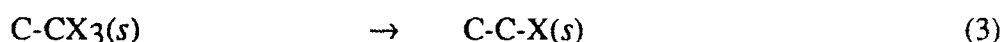
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substrate temperatures. There is no obvious nucleation requirement and therefore extremely high nucleation densities on non-diamond substrates may be achievable.

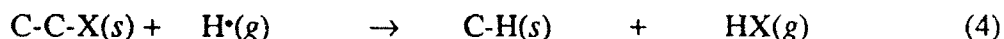
As described in detail elsewhere (2), our ALE method involves alternating cycles of halocarbon radicals and atomic hydrogen. In the first half of the cycle, halocarbon radicals impinge on a hydrogen-terminated diamond surface, first abstracting surface hydrogen atoms and then sticking to the radical (dangling-bond) site produced:



where X is a halogen atom (F or Cl). Adsorbed halocarbon species then undergo surface decomposition or rearrangement reactions to produce a halogen-terminated surface:

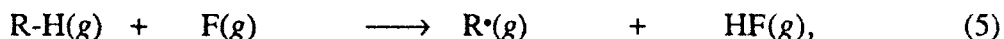


Reactions (1)-(3) should be self-terminating because activation energies for abstraction of halogen atoms by carbon- and silicon-centered radicals are much higher than for abstraction of hydrogen. In the final step of the cycle, the surface halogen atoms are stripped off by abstraction reactions of incoming hydrogen atoms and replaced by hydrogen:



Because etching of diamond by atomic hydrogen is very slow, reaction (4) should also be self-terminating.

Growth experiments were performed in an ultrahigh-vacuum-compatible CVD/ALE reactor that has been described previously (2) and is illustrated schematically in Fig. 1. Thermally-dissociated fluorine atoms abstract hydrogen atoms quantitatively from precursor molecules injected in excess downstream from the F source where the gas density is high enough for collisions, producing radicals with nearly complete chemical specificity:



where R = H, CH₃ or CX₃, corresponding to injection of H₂, CH₄, or CHX₃. We have also performed some experiments using C₂H₂ as a precursor, which probably reacts primarily via an addition reaction, generating a fluorovinyl radical:



The radicals (and HF) formed downstream of the F-atom source flow under nearly molecular flow conditions to the substrate.

Because only a handful of groups in the world have successfully demonstrated diamond growth at pressures below 1 Torr (3) and because this growth method is completely new, we deemed it essential to demonstrate growth by CVD (continuous reactant fluxes) and to optimize the experimental parameters before attempting ALE. In this work the fluorine was dissociated in resistively-heated nickel tubing at temperatures of 600-650 °C. We employed flow rates of 1-10 sccm of F₂, 5-60 sccm of H₂, and 5-60 sccm of

CH₄ or C₂H₂. Previous experiments utilized CHCl₃ as a precursor (2,4) and experiments with CHF₃ are underway. The chamber pressure rose to 10⁻³ - 10⁻¹ Torr during growth. We previously obtained evidence for diamond growth on diamond (100) substrates using CHCl₃ or CH₄ as precursors (2,4), including thickness increases and surface morphological features suggestive of growth. However, we sought more definitive evidence for diamond growth, and in the present work we have used polycrystalline copper and nickel wires seeded with 5-8 μm natural diamond grit as substrates, held at temperatures between 500 and 600 °C.

Particle and film deposits were characterized by Raman spectroscopy, scanning electron microscopy (SEM), and electron microprobe x-ray fluorescence (Cameca Camebax SX50).

RESULTS AND DISCUSSION

Preliminary evidence of *de novo* diamond growth was obtained following growth for 20 hours on a diamond-seeded copper substrate held at 600 °C using C₂H₂ as the precursor. Platelets with square faces and ledge features at 90° orientations, several microns in size, were observed by SEM, as shown in Fig. 2. Electron microprobe x-ray fluorescence analysis indicated that no elements were present on the platelets except for carbon, and wavelength-dispersive spectra identified the particles as diamond. When high energy electrons strike a substrate, x-ray photons are emitted whose energies are characteristic of the elements present. Carbon in different bonding environments emits x-ray photons differing in energy by an eV or more, and hence can be distinguished by wavelength-dispersive spectroscopy (WDS) (5). WDS spectra of graphite and diamond obtained using the instrument standards are shown in Fig. 3. The WDS spectra of graphite and diamond are readily distinguishable, peaking at 275.7 and 277.5 eV, respectively, a 1.8 eV shift. Fluorescence from the platelets exhibited a peak at 277.6 eV, indicating that the platelets are diamond, or at least are predominantly sp³ bonded. We are unaware of previous reports of such a platelet morphology for diamond grown by CVD. This unusual morphology presumably stems from the nucleation mechanism, which is unknown at present.

We have also obtained evidence for diamond growth using CH₄ as the precursor. Particles observed after growth for 12 hours on a diamond-seeded nickel substrate held at approximately 600 °C are shown in Fig. 4. No evidence for *de novo* diamond nucleation and growth was seen in this case. However, we found that the diamond seed particles had become enlarged substantially, indicating diamond growth. SEM analysis of many samples indicated that *all* the diamond grit particles used as seeds are between 5 and 8 μm in diameter, as specified by the vendor. Therefore, the appearance of numerous particles up to 10-20 μm in size on the sample shown in Fig. 4 indicates that diamond growth occurred. Further characterization of this sample is underway. This result, diamond growth from F/F₂ + CH₄ + H₂, bears at least a superficial resemblance to the atmospheric pressure diamond growth process reported by Patterson *et al.* (6). However, the pressure

regime is very different, only a small fraction of the fluorine was dissociated at the higher pressure, and the growth mechanisms are probably quite different in the two cases.

Further diamond growth experiments are underway in our laboratory to define the appropriate parameters for ALE growth of diamond. In order to optimize the ALE process, it is necessary to determine the growth rate per cycle and adjust the process variables so as to reach a plateau in parameter space, that is, where the growth rate per cycle is relatively insensitive to flux, temperature, etc., characteristic of self-limiting growth (1). We plan to utilize *in situ* Fizeau interferometry (7) for this purpose.

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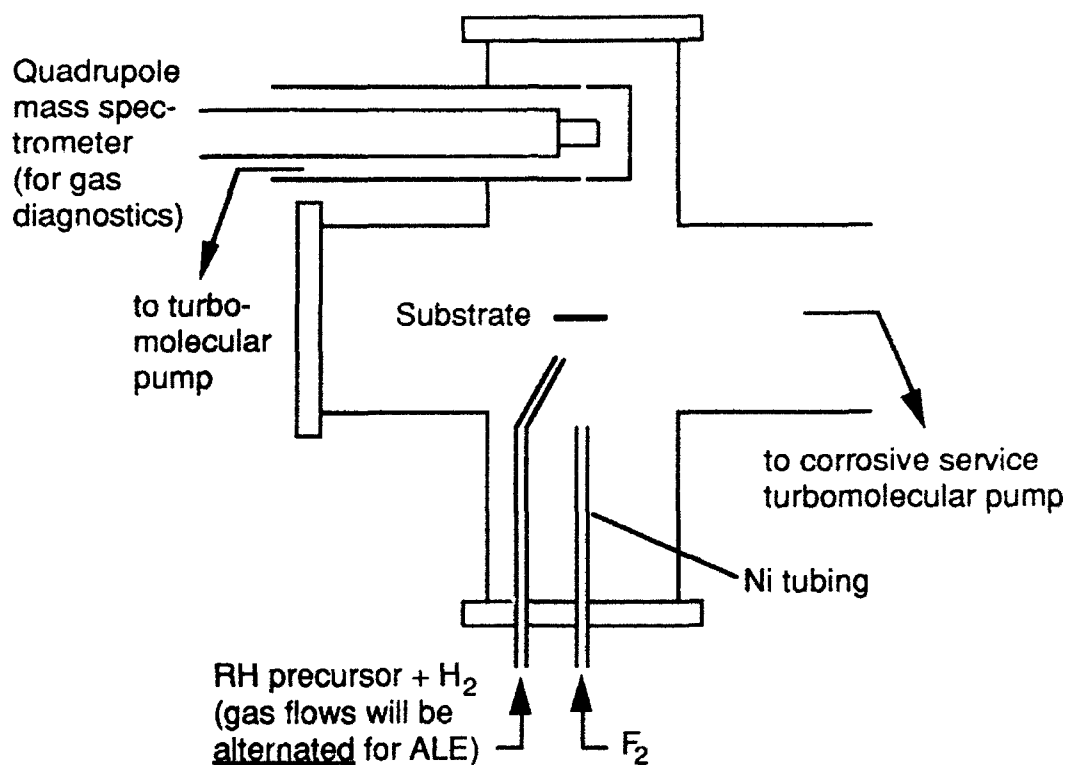


Fig. 1. Schematic of ultrahigh-vacuum-compatible radical ALE growth apparatus. Precursor molecules are injected into a stream of fluorine atoms generated by thermal dissociation in Ni tubing, producing radicals + HF.

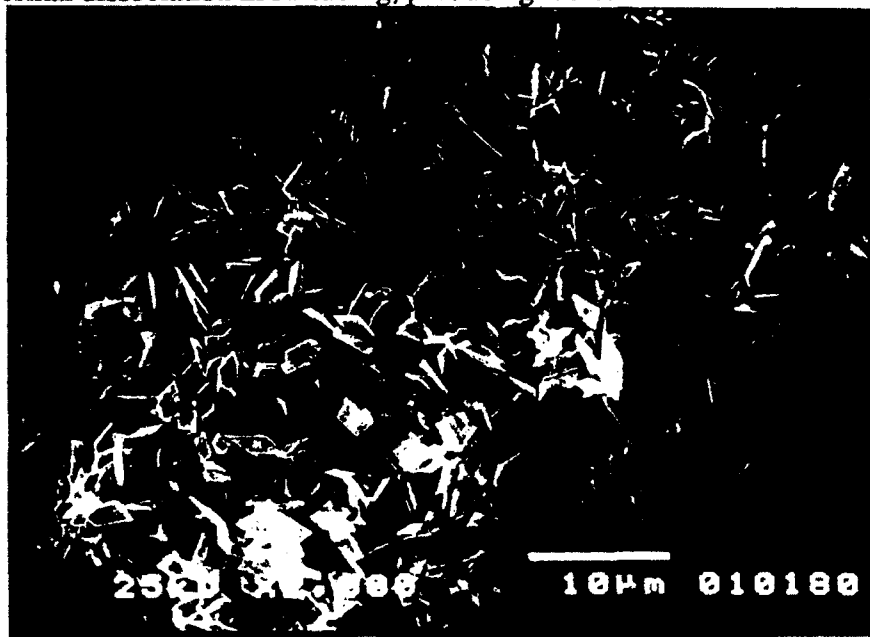


Fig. 2. Scanning electron micrograph of diamond platelets grown for 20 hours from $F/F_2 + H_2 + C_2H_2$ on a copper substrate at approximately 600 °C.

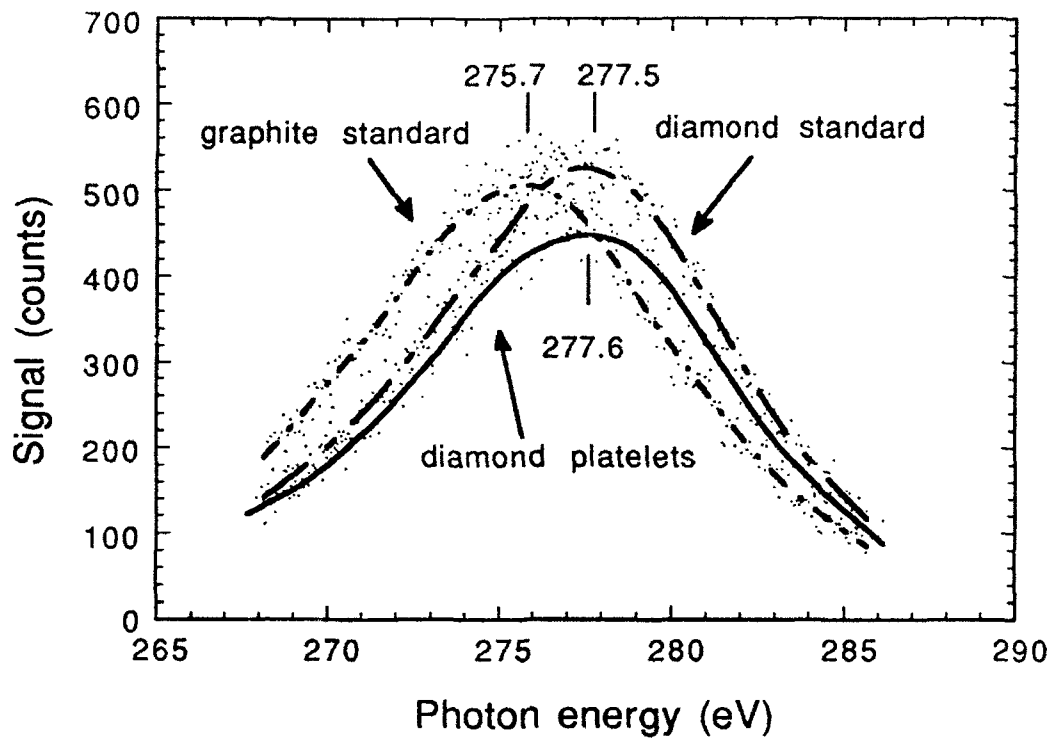


Fig. 3. Wavelength dispersive spectra of diamond and graphite standards and of diamond platelets shown in Fig. 2.

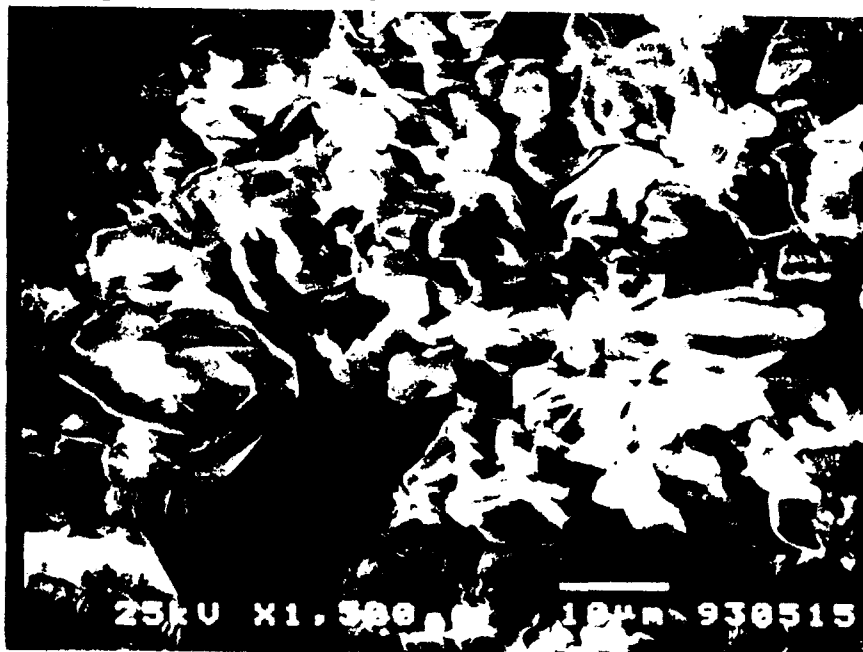


Fig. 4. Scanning electron micrograph of diamond grown for 12 hours on 5-8 μm diamond seeds from $\text{F}/\text{F}_2 + \text{H}_2 + \text{CH}_4$ on a nickel substrate at $\approx 600^\circ\text{C}$.